

# PATENT SPECIFICATION

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## (54) PREPARATION OF COLOURED RESINS

- (71) We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301, East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to a process for preparing coloured resins using certain non-toxic water-soluble dyes, the invention relates especially to a process for preparing colour-fast particles of substantially water-impervious, cross-linked thermosetting resins using non-toxic water-soluble dyes.
- Colour has been acknowledged to play an important role in consumer acceptance of many products. In many cases colour has been used to distinguish particular products in the market place and to identify products having particular distinct properties. Coloured products are usually formulated by merely adding the desired dye to the other components prior to the mixing stage of the process.
- As the dyes current utilized in toothpaste are all water-soluble, and varying large amounts of water are present in toothpaste, the desired colour spreads and uniformly colours the entire product. An alternative means of uniformly colouring a toothpaste is to disperse uniformly in the paste very small particles of insoluble coloured material which acts as a pigment. Although this material is discerned as discrete coloured particles when the paste is examined under a magnifying lens, to the naked eye the paste has a uniform coloured appearance. It is, of course, essential that the particles which serve as pigments be coloured with a dye which is acceptable for use in products which may be ingested.
- Although overall coloured effects as described above can be quite pleasing to the consumer, one of the most attractive and effective uses of colour is the speckled effect which can be achieved by incorporating a minor proportion of particles which are large enough to be easily discerned with the naked eye into a composition of contrasting colour. By uniformly dispersing relatively large coloured particles, a product having numerous, discrete, well-defined centres of contrasting colour or colours randomly but uniformly distributed therethrough is attained which presents a striking and highly distinctive appearance.
- Granular detergent compositions containing coloured speckles are well-known and are disclosed, for example, in British Patent Specification No. 808,668. The speckling effect in granular detergents is achieved by merely dyeing a minor proportion of the detergent granules. Such coloured granules could not be used to colour or speckle toothpaste for obvious reasons. Coloured thermosetting resin particles have been disclosed for use in colouring thermoplastic resin compositions in U.S. Patent 3,095,400; however, these particles are coloured with water-insoluble dyes or pigments and would not be suitable for use in a toothpaste. The use of substantially colourless synthetic resins as abrasive polishing agents in dentifrice compositions has also been disclosed in the prior art, see, e.g., U.S. Patent 2,130,034 and U.S. Patent 3,070,510. The art does not disclose the use of dyed synthetic resins in dentifrice compositions, nor does it

suggest a method for colouring such resins with water-soluble dyes.

To be useful in colouring a toothpaste, either uniformly as a pigment or speckling by agglomerating the particles to a clearly visible size, dye must not be leached from the particles, i.e., the particles should not bleed colour, and streak the entire dentifrice. Since the dyes permitted for use in dentifrice products by the U.S. Food and Drug Administration are all water-soluble and toothpastes generally contain substantial quantities of water, it has not hitherto been possible to prepare acceptable colour-fast particles for such use.

It has now been discovered that coloured particulate resins can be prepared with certain non-toxic, water-soluble dyes and that these resins are especially suited for use as a toothpaste pigment or in speckling toothpaste when the particles are agglomerated in accordance with the process described in copending Application No. 31138/70 (Serial No. 1,319,992).

The present invention provides a process for the preparation of a coloured, substantially water-impervious, cross-linked synthetic resin which comprises polymerization, in an aqueous solution, of a precursor or precursors of the resin and dissolving a water-soluble, non-toxic dye (as hereinafter defined) in the aqueous solution prior to the completion of the said polymerization.

For the purposes of this specification, a "non-toxic dye" is defined as a dye that, for the time being, is certified for use in foods, drugs and cosmetics by the United States Food and Drug Administration (i.e. an "F D & C" dye).

Unexpectedly, it has been found that resin particles formed by polymerization in the presence of the dye solution take on the colour of the dye to form coloured resin particles which are extremely colour-fast. When employed uniformly to colour a toothpaste base a sufficient quantity of the resin pigment particles can be used to additionally function as an abrasive polishing agent so long as the particle size is within a suitable range as hereinafter specified.

The resins which when dyed in accordance with this invention are suitable for colouration of dentifrices, especially toothpastes, are substantially water-impervious, cross-linked, thermosetting, highly polymerized resins, the monomers or precursors of which are soluble in water and can be polymerized in aqueous solution. A thermosetting resin is one which solidifies on heating and cannot be remelted. This property arises from the formation of cross-links between polymer chains during the chemical reaction which is promoted by heat or chemical means. The resulting three-dimensional network of polymers is the type of structure which is required to achieve the desired

colour-fast character when formed in a dye solution in accordance with this invention.

The expression "substantially water-impervious" is applied to resins which do not take up appreciable water on prolonged contact. Preferably water absorption in 24 hours at 25°C. according to ASTM Test D-570-57T is less than about 1%. The absorption of water leads to swelling and softening of the resin particles, and leaching of the dyes. Casein resins are examples of a type of thermosetting plastic which is unsatisfactory because of relatively high water absorption. While it is not intended that this invention be limited by a particular theory, it is believed that dye molecules are entrapped within the three dimensional cross-linked structure of thermosetting resin structure and by virtue of the water-impervious character of these resins the entrapped molecules are essentially "water-proof" and remain colour-fast even in the presence of water.

Preferred types of thermosetting cross-linked synthetic resins which can be dyed in accordance with this invention include the highly polymerized urea-formaldehydes, melamine-formaldehydes, melamine-urea-formaldehydes, and phenol-formaldehydes. These resins can be prepared either by polymerizing the corresponding monomers or by further polymerizing water-soluble lower molecular weight resins formed from these monomers. The low molecular weight water-soluble resins which can be used to prepare the final insoluble resin particles are prepared in normal commercial practice by polymerization promoted by heat, with or without a catalyst present. Pressure is sometimes used with heat in commercial practice during polymerization, such as in moulding operations. The finished resin is formed by acid catalyzed polymerization wherein the water-soluble monomer or low molecular weight resin is reacted in aqueous solution. The type of acid catalyst is not critical, but strong acids such as sulphuric acid are preferred. The polymeric precipitate thus formed is dried and ground and/or screened to appropriate particle size.

A preferred embodiment comprises (1) forming an aqueous solution of a water-soluble non-toxic dye and a water-soluble reaction product of melamine and formaldehyde, the molar ratio of formaldehyde to melamine in said reaction product being in the range from 2:1 to 4:1, and the weight ratio of the said reaction product to water being in the range of 1:2.3 to 1:3.5; and (2) acidifying the resulting solution at a temperature of 50°C to 85°C with agitation in an amount no more than that sufficient to provide a substantially uniform mixture and to effect polymerization to form the resin.

Preferably, the resin precipitate is subjected to further heat treatment to promote an even higher degree of polymerization and

- cross-linking, either before or after reduction to appropriate particle size. This latter heat treatment makes the resin extremely rigid and brittle, properties which render the resin useful for dental cleaning and polishing.
- It is essential that the polymeric material be in particulate form for such purposes as the colouring of toothpaste. The resin may precipitate in particulate form from the acid-catalyzed polymerization reaction, in which case, particles of the desired size, as set forth hereinafter, can be separated by screening, and the remaining particles can be reduced to the desired size by conventional grinding methods such as impact, ball and tube milling. If the resin precipitates in bulk, the entire mass can be ground and screened to obtain the desired particle size. If a final heat treatment is used to impart abrasive properties to the resin, the grinding to desired particle size can be before or after heat treatment but it is preferred that it be done before heat treatment, since this will reduce the time necessary for heat treatment.
- An indication of the types of cross-linked, thermosetting resins which are suitable for use in this aspect of the invention has been given. So long as the resin meets the requirements set forth, i.e. the monomer or low molecular weight resin precursor is water-soluble, and the finished resin is impermeable to water, cross-linked and thermosetting, the exact composition of the resin has little effect on its performance as a colourant for toothpastes.
- The resinous materials of the invention are preferably composed of particles substantially all of which have a diameter of less than 500  $\mu$ , and if the resin is to be used as a cleaning and polishing agent, preferably less than 50  $\mu$ . Larger particles tend to feel gritty in the mouth and to stick between the teeth. The mean diameter of the particles is desirably from about 5  $\mu$  to 40  $\mu$  and preferably 5  $\mu$  to 20  $\mu$  for optimum abrasive properties. Larger particles can be used in the preparation of speckle agglomerates as will be more fully considered hereinafter. The particle diameters referred to herein are determined by microscopic measurements using a calibrated eyepiece.
- Examples of suitable F D and C dyes are:
- F D & C Blue No. 1. (Brilliant Blue FCF—disodium salt of 4 - ([4 - (N - ethyl - p-sulphobenzylamino)phenyl](2 - sulphonium-phenyl)methylene)[1 - (N - ethyl - N - p-sulphobenzyl) -  $\Delta^{2,3}$  - cyclohexadienimine]);
- F D & C Blue No. 2 (Indigotine—disodium salt of 5,5'-indigotindisulphonic acid);
- F D & C Green No. 1 (Guinea Green B—monosodium salt of 4 - [- (N - ethyl - p - sulphobenzylamino)diphenylmethylene] - [1 - (N - ethyl - N - p - sulphoniumbenzyl) -  $\Delta^{2,3}$  - cyclohexadienimine]);
- F D & C Red No. 2 (Amaranth—trisodium salt of 1 - (4 - sulpho - 1 - naphthylazo)- 2 - naphthal - 3,6 - disulphonic acid);
- F D & C Red No. 3 (Erythrosine—disodium salt of 9 - o - carboxyphenyl- 6 - hydroxy - 2,4,5,7 - tetraido - 3 - isoxanthone);
- F D & C Red No. 4 (Ponceau SX—disodium salt of 2 - (5 - sulpho - 2,4-xylylazo) - 1 - naphthol - 4 - sulphonic acid);
- F D & C Yellow No. 5 (Tartrazine—trisodium salt of 3 - carboxy - 5 - hydroxy- 1 - sulphophenyl - 4 - p - sulphophenyl-azopyrazole);
- F D & C Yellow No. 6 (Sunset Yellow FCF—disodium salt of 1 - p - sulphophenylazo - 2 - naphthol - 6 - sulphonic acid);
- F D & C Violet No. 1 (Acid Violet 6B—monosodium salt of 4 - ([4 - (N - ethyl - p - sulphobenzylamino)phenyl] - [4 - (N - ethyl - p - sulphoniumbenzylamino) phenyl] methylene) - (N,N,dimethyl -  $\Delta^{2,3}$  - cyclohexadienimine);
- The amount of dye employed in the present process depends on the relative chroma desired and the colour characteristics of the selected dye. Generally, the concentration of the dye can be from about 0.001% to about 30% by weight of the reaction mixture. The primary attributes of colour are (a) hue, (b) brightness or value, and (c) saturation, purity or chroma. In the practice of this invention the hue may be selected from the whole range derivable from the non-toxic water-soluble dyes disclosed herein. In the Munsell system of colour notation (see the Munsell Book of Color, Munsell Color Co., Inc., Baltimore, Maryland, 1929), the finished resin preferably has a Munsell Value of about 4 to 7 and a Munsell Chroma of more than 4.
- Using another colorimetric system (see the Journal of the Optical Society of America, 1940) the apparent reflectance of the resins is preferably about 0.20 to about 0.45 and the excitation purity, while varying somewhat with the hue, should be above 20%.
- Thus, the concentration of dye employed in the present process is preferably sufficient to yield the indicated value and chroma.
- The present invention is illustrated in and by the following Examples.
- Unless otherwise specified, references to percentages and parts in this specification refer to percentages and parts by weight.
- Example I
- Green urea-formaldehyde resin particles were prepared by the following process;
- 56.065 parts of distilled water were placed in a reaction vessel equipped with a steam jacket, agitator and thermocouple. Agitation was commenced and the water was heated to a temperature of 155°F. 13.235 parts of urea



were dissolved in the water and the temperature of the solution dropped to 120°F. To the urea solution were added 0.025 parts of powdered FD&C Blue No. 1 dye and 0.025 parts of FD&C Yellow No. 5 dye and mixing was continued until the dyes were completely dissolved. 30.615 parts of a 37% stabilized formaldehyde solution were added to the dyed urea solution, followed by the slow addition of 0.031 parts of concentrated sulphuric acid. The reaction mixture was then brought to a temperature of 120°F and the reaction began, as evidenced by a sudden lightening in colour of the reaction mixture. As the reaction proceeded, the temperature of the reaction mixture increased to 150°–160°F during the first 10 minutes.

When the reaction temperature stabilized, the mixture was cooled to 120°F and reacted at this temperature for two hours with constant agitation. The mixture was then placed in a filtering centrifuge and the resulting solids cake was washed with water and placed in a dryer. The solids cake was dried to a moisture content of less than 10% at a temperature of 220°F. The dried resin was pulverized to reduce all lumps and the mass was screened through a U.S.B.S. No. 40 test sieve (420  $\mu$ ). The coloured resin particles were further reduced in size by pulverizing by ball milling to an average particle diameter of 10 microns. The resulting particles were green in colour (Munsell Value 4–7, Munsell Chroma > 4) and were found to be colour-fast in the presence of water.

In the foregoing process, the critical components in the reaction are the dye, urea, formaldehyde and acid. For a practical reaction to take place, all of the reactants must be present in the reaction mixture. Thus, the order of addition of the reactants makes no practical difference. It is preferred, however; that the dye be added to the mixture before the last of the reactants.

While the dye in this example was added in powder form, it can also be dissolved in water prior to addition to the reaction mixture and added as a concentrated aqueous solution. The total amount of water used in the reaction mixture should be adjusted for the amount present in the dye solution if the dye is added in this manner. The dyes employed in this example can be replaced by any one or more of the FD&C dyes recited in the foregoing disclosure to secure colour-fast resin particles which are identical to those of the above example except in colour.

The 37% formaldehyde solution employed in this example was stabilized with 6–8% of methanol. Formaldehyde is commercially available in the form of methanol-stabilized (1–12%) aqueous solutions of formaldehyde at concentrations of 37% to 50% and in the form of a white crystalline powder (paraformaldehyde). Any of these forms can be used

in the present process. However, if paraformaldehyde is used it must be dissolved in water with the aid of a strong base and greater concentrations of acid, e.g. sulphuric acid, will be required to catalyze polymerization of the urea and formaldehyde.

The catalytic effect of the acid depends upon the hydrogen ion concentration in the reaction mixture and this in turn depends upon the degree of dissociation of the acid and its concentration in the reaction mixture. Thus, any acid can be used in place of sulphuric acid in the present process, but if weaker acids such as acetic acid are employed, larger amounts are required. Preferably, the strong mineral acids are used.

While the water in this process was heated to a temperature of 155°F prior to the addition of urea, this is not essential. Without preheating the urea addition will lower the water temperature to below 120°F, the preferred temperature for initiating the reaction. However, as the reaction proceeds the temperature of the mixture will rise to 150° to 160°F.

The reaction time can be varied over a wide range. It should be long enough to secure a sufficient yield, usually at least about 30 minutes, but reaction times greater than about 3 hours will not substantially increase yields and the reaction should be discontinued within this time.

Coloured melamine-formaldehyde resin can be prepared in accordance with this invention by modifying the process disclosed in U.S. Patent 3,251,800, by dissolving an FD&C dye in the first reaction step. Thus, coloured resins of this type are secured in the following process.

#### Example II

3000 parts of a water-soluble melamine-formaldehyde resin (Resimene 817, a dry white powder supplied by Monsanto Chemical Co.), 6 parts of FD&C Red No. 2, and 150 parts of sodium chloride are dissolved in 7000 parts of water and heated to 60°C. A solution of 240 parts of concentrated nitric acid in 6500 parts of water at 60°C is poured rapidly into the dye-resin solution. The resulting mixture is stirred with two revolutions of a spatula and the swirling of the mixture is stopped quickly by lowering into the mixture a radiating set of baffle plates. After 10 minutes the resulting resin gel is cut into sections and removed from the reaction vessel. Water is pressed from the gel, after which the gel is dispersed in water and filtered. The filtered gel is spread in a thin layer and dried in an oven at 100°C. The dried resin is then heat cured for 16 hours at 110°C. The cured resin, consisting of agglomerates of small red particles, is placed in a ball mill and milled to a particle size ranging from 5 to 15 microns average diameter. The resulting highly cross-linked, water-impervious thermosetting red

resin particles are colour-fast and do not have colour leached out when placed in water. This resin has a Munsell Value of from 4—7 and a Munsell Chroma greater than 4. Similar results are secured when the FD&C Red No. 2 dye is replaced with an equivalent amount of any of the FD&C dyes recited in the preceding disclosure.

Coloured melamine - urea - formaldehyde resins can also be prepared in accordance with this invention by the method of U.S. Patent 3,251,800 referred to above, as follows:

#### Example III

100 parts of a commercial, water-soluble melamine-urea-formaldehyde resin (Resin TS 5913, a dry white powder made by the Monsanto Chemical Company) estimated to have a melamine:urea:formaldehyde ratio of 1:1:4.5, and 2.5 parts of FD&C Violet No. 1 are dissolved in 250 parts of water at 60°C. 20 parts of concentrated hydrochloric acid (38%) are poured into and mixed with the dye-resin solution. Movement of the mixture is stopped and it then sets to a gel. After the gel becomes firm (generally a few minutes), it is removed from the reaction vessel and heat cured for 16 hours at 150°C. The cured resin is placed in a ball mill and reduced to particles having an average diameter of approximately 10 microns. The resulting water-impervious, highly cross-linked thermosetting resin particles are violet in colour and the colour is not leached out when the particles are placed in water. This resin has a Munsell Value of from 4—7 and a Munsell Chroma greater than 4.

Similar results are attained when the FD&C Violet No. 1 dye of this example is replaced by an equivalent amount of another non-toxic water-soluble dye such as those FD&C dyes disclosed herein.

Coloured particles of a phenol-formaldehyde resin are prepared by dissolving a FD&C approved water-soluble dye in the aqueous solution of formaldehyde prior to reacting the formaldehyde with phenol. The preparation of essentially colourless resins by reacting formaldehyde with phenol is described by La Follette in U.S. Patent 3,357,950. The following example illustrates the preparation of coloured resins by modifying the La Follette process in accordance with the present invention.

#### Example IV

400 parts of formaldehyde (37% aqueous solution stabilized with 11% methanol) are placed in a reaction vessel. 4 parts of FD&C Blue No. 1 are dissolved in the formaldehyde solution. To this solution are added 200 parts of phenol and 20 parts of sodium hydroxide. The solution is mixed and heated to a temperature of 94—97°C. for 45 minutes.

5 parts of maleic anhydride, 63 parts of citric acid and 100 parts of demineralized

water are slowly added to the reaction mixture while maintaining the temperature at about 95°C. Heat is then applied to dehydrate the mixture at a temperature of 105°C for 40 minutes. The solid residue is removed from the reaction vessel and placed in boiling water for two hours. After this boiling cure the solid is placed in 10,000 parts of water at 25°C to which has been added 50 parts of sulphuric acid. The water is then removed and the solid is dried and cured at 85°C in a forced air oven for 16 hours.

The resulting blue phenol-formaldehyde resin is ball milled to a particle size of 5 to 40 microns and these particles are placed in boiling water for one hour and then air dried at room temperature. The final product is a colour-fast blue, highly polymerized cross-linked, thermosetting particulate phenol-formaldehyde resin. The Munsell Value of this resin is from 4—7 and the Munsell Chroma is greater than 4.

Toothpastes typically comprise a cleaning and polishing agent, a sudser, a humectant, a thickener or binder, flavouring and sweetening agents and water. In the absence of a dye or other colouring substance these components yield a product which is generally white in colour. Indeed, most of the commercially available toothpastes are white. Toothpastes of other colours are available and there are prepared by dissolving an FD&C dye in the water component of the paste in the mixing process. When the coloured resin particles of the foregoing examples are employed as cleaning and polishing agents, the coloured particles act as a pigment which uniformly colours the toothpaste to a desired hue. The total amount of resin particles present in toothpastes for cleaning and polishing purposes is from about 10% to about 90% and preferably from about 20% to about 60% by weight. The depth of colour hue attained depends upon the degree of colour of the particles per se and their concentration in the finished paste formula.

A toothpaste composition may be prepared containing a representative coloured resin which serves both as a pigmentation and cleaning and polishing agent, having the following composition:

|                                | Percent by Weight |     |
|--------------------------------|-------------------|-----|
| Green urea-formaldehyde resin* | 25.0              | 120 |
| Glycerine                      | 30.0              |     |
| Hydroxyethylcellulose          | 1.5               |     |
| Sodium lauryl sulphate         | 1.5               |     |
| Flavour                        | 0.9               |     |
| Saccharin                      | 0.2               | 125 |
| Stannous fluoride              | 0.4               |     |
| Water                          | Balance           |     |

\* Prepared in accordance with Example I.

This toothpaste has a uniform green colour which is free from dye streaks. It is effective in cleaning teeth with a minimum of abrasion.

5 The resin employed in the above toothpaste is replaced with the resins secured in Examples II, III and IV respectively and uniformly coloured products are attained.

10 Agglomerates of the resins of the foregoing Examples may be prepared in accordance with the methods disclosed in the aforementioned copending Application No. 31138/70 (Serial No. 1,319,992) and these agglomerates may be used to prepare a speckled toothpaste with good results.

# 15 WHAT WE CLAIM IS:—

1. A process for the preparation of a coloured, substantially water-impervious, cross-linked synthetic resin which comprises polymerization, in an aqueous solution, of a precursor or precursors of the resin and dissolving a water-soluble, non-toxic dye (as hereinbefore defined) in the aqueous solution prior to the completion of the said polymerization.

25 2. A process according to claim 1 wherein the said precursor(s) is/are caused to polymerise by heating and/or addition of an acid.

3. A process according to claim 1 or 2 wherein the resin is a condensate of melamine and formaldehyde.

4. A process according to claim 1 or 2 wherein the resin is a condensate of melamine, urea and formaldehyde.

5. A process according to claim 1 or 2 wherein the resin is a condensate of urea and formaldehyde.

6. A process according to claim 1 or 2 wherein the resin is a condensate of phenol and formaldehyde.

40 7. A process according to any of claims 1 to 6 wherein the said precursors are water-soluble monomers.

8. A process according to any of claims 1 to 6 wherein the said precursor is a water-soluble resin capable of further cross-linking.

45 9. A process according to claim 1 which comprises (1) forming an aqueous solution of a water-soluble non-toxic dye and a water-soluble reaction product of melamine and formaldehyde, the molar ratio of formaldehyde to melamine in said reaction product being in the range from 2:1 to 4:1, and the weight ratio of the said reaction product to water being in the range of 1:2.3 to 1:3.5; and

55 (2) acidifying the resulting solution at a tem-

perature of 50°C to 85°C with agitation in an amount no more than that sufficient to provide a substantially uniform mixture and to effect polymerization to form the resin.

10. A process according to claim 5 which comprises (1) forming an aqueous solution of a water-soluble non-toxic dye, urea and formaldehyde; (2) acidifying the resulting solution with an amount of a strong mineral acid sufficient to catalyse polymerization and (3) removing the precipitated resin secured in the foregoing step and drying same.

11. A process according to any of claims 1 to 10 wherein the water-soluble non-toxic dye is present at a concentration of 0.001% to 30% by weight of the aqueous reaction mixture.

12. A process according to any of claims 1 to 11 wherein the dye imparts to the synthetic resin a Munsell Value of 4 to 7 and a Munsell Chroma of greater than 4.

13. A process according to any of claims 1 to 12 wherein the resin is ground to a particle size of less than 500 microns.

14. A process according to claim 13 wherein the resin is ground to a particle size of less than 50 microns.

15. A process according to any of claims 1 to 14 wherein the resin is ground to a mean particle diameter of 5 to 40 microns.

16. A process according to claim 15 wherein the resin is ground to a mean particle diameter of 5 to 20 microns.

17. A process according to any of claims 13 to 16 wherein the resin is heated after grinding, whereby the particles are rendered more brittle.

18. A process according to claim 1 of preparing coloured, substantially water-impervious, cross-linked, synthetic resin substantially as hereinbefore described in the Examples.

19. A coloured synthetic resin when prepared by a process according to any of claims 1 to 18.

20. A dentifrice composition comprising particles of a coloured synthetic resin according to claim 19 in admixture with a carrier suitable for use in the oral cavity.

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